

Characterization of Coal Products by Mass Spectrometry

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I. Introduction and Background

In studies on the organic chemistry of coal, the researcher, unfortunately, is unable to examine a complete coal molecule. He must instead be content to analyze bits and pieces of coal molecules produced by solvent refining, liquefaction, pyrolysis, or extraction. Knowledge of the composition of these pieces helps in understanding the organic chemistry of coal and is vital for the development of coal liquefaction processes and the further upgrading of the liquefaction products.

Mass spectrometry is the prime technique used in our laboratories (1,2) and in other laboratories (3) to determine the composition of the very complex mixtures derived from coal. Petroleum fractions have been analyzed by mass spectrometry (MS) for over 30 years. As heated inlet systems evolved (4,5) and instrumental resolving power increased, MS was applied to higher boiling ranges and more complex mixtures. When research in coal liquefaction began in our laboratories about 10 years ago, we had well-developed instrumentation, data handling procedures, and quantitative analyses for petroleum (6,7). Extension of these techniques to coal products required only minor changes and extensions (8,9). In this paper we describe some of the MS procedures we use and give some typical examples of analyses.

II. Equipment and Data Handling Procedures

A very repeatable low resolution instrument is used for streams in which the major components have been previously identified. The unseparated naphtha boiling range, separated saturate fractions, and mid-boiling range samples (when detailed knowledge of the hetero-atom components is not required) fall in this category. For mid-boiling and high-boiling fractions requiring more complete breakdown of aromatic, hydroaromatic, and aromatic hetero-compounds, spectra are obtained on a high-resolution double focusing instrument.

Both of the instruments are automated. A digital readout system senses peaks and converts analog signals to digital signals, records digital data on printed paper tape and on magnetic tape, and a larger computer reads the data from the magnetic tape and further processes it employing proprietary computer programs. A list of the equipment is shown below:

Item	Manufacturer	Model
Low Resolution MS	Consolidated Electrodynamics Corp.	21-103C
High Resolution MS	Associated Electrical Industries, Ltd.	MS50
MS Readout System	Columbia Scientific Industries	CSI-260
Printer	Mohawk Data Systems	2016
Computer	International Business Machines	370

III. Methods and Results

A. Naphtha Boiling Range

High ionizing voltage, low resolution spectra are adequate to determine paraffins, naphthenes, 2-ring naphthenes, C₆-C₁₁ benzenes, C₉-C₁₀ indanes and

tetralins, C₉-C₁₀ indenes, C₁₀-C₁₁ naphthalenes, and C₁₀-C₁₂ phenols in the C₅ to 450°F boiling range. The calibration data were derived primarily from scans of pure compounds and assembled in a 20 component matrix. A summary analysis is given in Table I.

Table I

<u>Component</u>	<u>Wt.%</u>
Total Saturates	76.6
Total Benzenes	13.9
Indanes/Tetralins	2.3
Indenes	0.1
Naphthalenes	0.0
Total Phenols	7.1
Total	100.0
Wt.Pct. Carbon	85.80
Wt.Pct. Hydrogen	13.09
Wt.Pct. Oxygen	1.11

With some assumptions regarding the molecular weight distributions of the paraffins and naphthenes, a useful elemental analysis can be readily calculated.

Occasionally more detailed data for the saturated components is desirable. A 42 component combined MS and gas chromatographic procedure determines the aromatic and phenolic components listed previously and further breaks down the paraffins into iso- and normal types by carbon number and the naphthenes into cyclohexanes and cyclopentanes by carbon number. Calibration data were obtained from pure compounds and from concentrates separated by molecular sieve and gas chromatography.

B. Higher Boiling Range Saturate Fraction

Fractions boiling above the naphtha range can be separated into saturate, aromatic, and polar fractions employing a modified version of the clay-gel adsorption chromatographic method, ASTM D-2007. The saturate fraction is analyzed by the high ionizing voltage MS method, ASTM D-2786. A typical analysis of a 430-950°F saturate fraction from a Synthoil product (10) is given in Table II.

Table II

<u>Compound Type</u>	<u>Wt.%</u>
Paraffins	34.2
1-Ring Naphthenes	18.4
2-Ring Naphthenes	16.3
3-Ring Naphthenes	14.6
4-Ring Naphthenes	10.3
5-Ring Naphthenes	3.0
6-Ring Naphthenes	1.1
Monoaromatics	2.1

Normal paraffins generally comprise the major part, 80-90%, of the total paraffins in coal liquefaction products and a lesser part in coal extracts. When a split between iso- and normal-paraffins is desired, gas chromatography rather than mass spectrometry is normally the method of preference in higher boiling

fractions. Iso-paraffins are not usually identified. However, we have recently identified the isoprenoid paraffins pristane, 2, 6, 10, 14-tetramethyl pentadecane, and phytane, 2, 6, 10, 14-tetramethyl hexadecane in coal extracts and liquefaction products. These components were separated and identified by gas chromatography, corroborated by MS (10).

Isoprenoid paraffins are used in organic geochemistry to group oils into "families" (11). It is possible that coals from different seams or deposits might be differentiated by the relative ratios of these isoprenoids or by the isoprenoid to n-paraffin ratio. Pristane is thought to be derived from the diterpenic alcohol phytol (12), that comprises about 30% of the chlorophyll molecule, and its presence and concentration might be related to the environment of the marsh in which a particular coal bed or seam was formed.

C. Higher Boiling Range Aromatic and Polar Fractions

If data on the saturate portion are not required, the aromatic and polar aromatic components are determined on the unseparated sample. This is done with a high resolution instrument operated in the low ionizing voltage mode (13). The same procedure can be applied to separated aromatic and polar fractions, and this is preferred if there is a significant concentration of polar components.

With low ionizing voltage electrons only those components containing double bonds, such as aromatics and olefins, are ionized and only the molecular ion is produced. Thus, the spectra, the spectral interpretation, and the calibration data are simplified, as there is no interference between components.

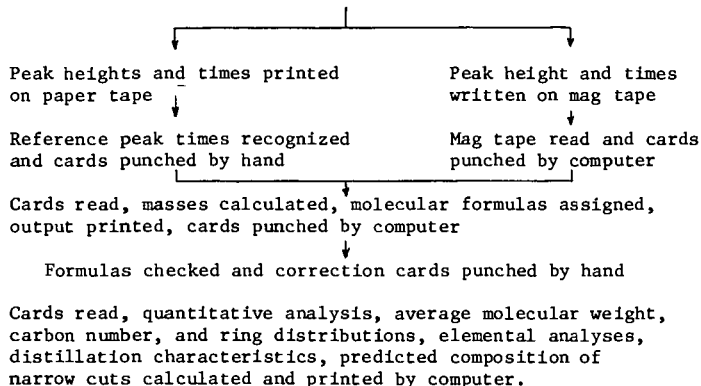
A full discussion of high resolution mass spectrometry is beyond the scope of this paper, so the technique will be described here only briefly. Different combinations to form molecules of the atomic species found in coal products will have different molecular weights. For example, from the atomic weights of the most abundant species given below one calculates the molecular weight of methyl

<u>Atomic Species</u>	<u>Atomic Weight</u>
Carbon	12.000
Hydrogen	1.0078
Oxygen	15.9949
Nitrogen	14.0031
Sulfur	31.9721

acenaphthene, $C_{13}H_{12}$, to be 168.0939, and the molecular weight of dibenzofuran, $C_{12}H_8O$, to be 168.0575. The high resolution MS resolves these two peaks having the same nominal molecular weight and the resolving power required is 4615 ($\text{Mass}/\Delta\text{Mass} = 168/0.036 = 4615$). Other molecules require even greater resolving power to separate, particularly those containing nitrogen or sulfur (14). The MS and its auxiliary apparatus must also provide data from which precise mass measurements can be calculated. By measuring the time at which each peak occurs in a repeatable logarithmic scan of the spectra and by introducing compounds having peaks at known masses, the masses of the sample peaks can be determined very precisely, and the mass determines the molecular formula.

The scheme we use from mass spectrometer to final quantitative analysis is given in the data flow scheme shown below. The MS, MS readout system, printer, computer, computer programs, and people are required.

Sample and reference compounds charged to high resolution MS



The most detailed information calculated from the high resolution spectra is the quantitative amount of each compound type at each carbon number. This tabulation is printed on 6 pages, 50 rows and 12 columns per page. This is more data than most engineers care to examine; therefore, summary tables, distributions, and other items are calculated from these detailed data. Excerpts from the compound type summary of a Synthoil product (10) are given in Table III. This is the initial summary made from the detailed data.

Table III

Compound Type	Wt. %	Average Mol. Wt.	Average Carbon No.	C Atoms in Sidechains
Alkyl Benzenes	1.74	160.8	11.9	5.9
Naphthalenes	11.02	176.4	13.5	3.5
Dibenzothiophenes	0.33	210.9	13.9	1.9
Fluorenothiophenes	0.16	241.2	16.4	2.4
Benzofurans	0.56	210.9	14.6	6.6
Dibenzofurans	2.55	255.0	16.1	4.1

The distribution of aromatic rings is a further summary which may be of value in refining of coal products. The ring distribution for the same product of Table III is shown in Table IV normalized to 100%, but the program also calculates and prints the same distribution normalized to the percent aromatics in the sample.

Table IV

	Hydrocarbons	Sulfur Comp.	Oxygen Comp.	Totals
Nonaromatics	0.0	0.144	0.0	0.144
1 Ring Aroms	20.960	0.517	2.235	23.712
2 Ring Aroms	36.919	0.611	3.465	40.996
3 Ring Aroms	15.644	0.153	2.202	17.999
4 Ring Aroms	12.388	0.067	1.470	13.925
5 Ring Aroms	1.997	0.020	0.208	2.225
6 Ring Aroms	0.856		0.084	0.940
7+ Ring Aroms	0.068			0.068
Totals	88.832	1.512	9.664	100.008

Additional calculated items, such as distillation characteristics (15), can be of great value to a researcher. If there is insufficient sample available for actual distillation, say from a bench-scale experiment, a few milligrams will suffice for a high resolution MS run. The calculated MS values, GC distillation, and 15/5 distillation are in good agreement.

The same high resolution scheme can also be applied to the polar fractions from the clay-gel separation. But the analysis of polars can become very tedious - the composition is much more complex as the polars contain many of the same hydrocarbon species as the aromatic fractions in addition to the polar hetero-aromatic oxygen, nitrogen, and sulfur compounds. In addition, our computer programs for some of these classes of components are not yet fully integrated into the final quantitative analysis program, and separate programs must be run and the results meshed. An indication of the complexity of the polar components in coal products is provided by a very small portion of spectra of the polar fraction of a Synthoil product given in Table V, in which some typical multiplets resolved by the high resolution MS are shown. The data were obtained at a resolving power of about 40,000.

Table V

Mass	Formula	Intensity	General Formula	Possible Structure
254.0764	$C_{16}H_{14}SO$	230	$C_nH_{2n-18}SO$	C_2 -Hydroxythiophenoacenaphthene
254.1306	$C_{17}H_{18}O_2$	822	$C_nH_{2n-16}O_2$	C_4 -Dihydroxyfluorene
254.1671	$C_{18}H_{22}O$	511	$C_nH_{2n-14}O$	C_6 -Hydroxyacenaphthene
381.1517	$C_{29}H_{19}N$	337	$C_nH_{2n-39}N$	C_2 -Dibenzoperylenide
381.1729	$C_{26}H_{23}NO_2$	219	$C_nH_{2n-29}NO_2$	C_5 -Dihydroxybenzochrysenide
381.2092	$C_{27}H_{27}NO$	363	$C_nH_{2n-27}NO$	C_7 -Hydroxydibenzcarbazole
381.2456	$C_{28}H_{31}N$	267	$C_nH_{2n-25}N$	C_9 -Chloranthridine
394.1357	$C_{30}H_{18}O$	110	$C_nH_{2n-42}O$	C_2 -Hydroxybenzocoronene
394.1569	$C_{27}H_{22}O_3$	225	$C_nH_{2n-32}O_3$	C_5 -Trihydroxybenzoperylene
394.1933	$C_{28}H_{26}O_2$	275	$C_nH_{2n-30}O_2$	C_6 -Dihydroxybenzochrysene
394.2295	$C_{29}H_{30}O$	507	$C_nH_{2n-28}O$	C_9 -Hydroxybenzopyrene

III. Conclusions

The national need to develop liquid fuels from coal to augment diminishing petroleum fuels is a challenge to the coal chemist. Analytical characterization of these coal liquids is a challenge to the analytical chemist. We believe that mass spectrometry, both low resolution and high resolution, plays an important role in responding to this challenge, and have given examples of the application of the technique to various coal product samples.

More detailed information on the use of high resolution mass spectrometry to analyze hetero-compounds in coal extracts and liquefaction products is given in our paper in the "Symposium on Refining of Coal and Shale Liquids," Division of Petroleum Chemistry, National ACS meeting, Chicago, 1977.

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